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Evaluating Protective Coatings and Metal Alloys in Acidic Geothermal Fluids Using Laboratory Techniques

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ABSTRACT

Internal corrosion of carbon steel pipes exposed to acidic geothermal fluids is a major problem in the geothermal industry that may be controlled through the use of suitable corrosion resistant materials and barriers. In this paper, the abilities of three (3) types of metal alloys (i.e. K55, A53 Gr. B and SS316) and seven (7) types of protective coatings (Brands A - G) to resist corrosion in low-pH geothermal brine ($pH_{25C} < 4.0$) were assessed using different analytical techniques in the laboratory. The sample coatings and alloys were subjected to immersion tests in low-pH geothermal brine at various temperatures and pressures (i.e. Rm. T-atm P, 70 °C-atm P and HT-HP) to simulate different operating conditions. Data on surface quality, corrosion rates and failure/corrosion mechanism of the test specimens after exposure were obtained using Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization Scans (PPS). Thermogravimetric Analysis (TGA) and X-ray Photoelectron Spectroscopy (XPS) were also utilized to characterize the resulting precipitates, while Scanning Electron Microscopy (SEM) was used to determine surface morphology. Results showed that EIS, PPS, XPS and SEM are good tools to use as standard analytical techniques for evaluation of coating and metal samples in the laboratory prior to field application.

Corrosion rates for the metal alloy specimens increased with temperature. SS316 alloy generated the highest corrosion rate after 5 hour immersion in low-pH brine both at Rm. T and at 250^{o}C. Precipitates found in solution and adherent to alloy surface were mostly composed of O, Si, Cl, C and trace amounts of metals. These appeared to provide inhibition in A53 Gr. B and K55 alloys but not in SS316 metal. PPS revealed that corrosion inhibition in A53 Gr. B and K55 alloys is controlled by the anodic reaction where iron component of metal is dissolved in the test media.

All types of coatings that were tested exhibited protective properties in acidic environment that showed decreasing trend with temperature. At higher temperatures, protection efficiencies of the coatings declined by ~20 – 50% while measured corrosion rates and visible coating defects (i.e. wrinkling and pinholing) increased. Utilization of these coatings may also induce deposition of precipitates composed of silica, oxides and inorganic salts inside the pipes.

1. INTRODUCTION

Geothermal fluids contain dissolved gases and solids whose thermodynamic behavior during utilization causes problems such as corrosion. The National Association for Corrosion Engineers' (NACE's) Corrosion Basics book defines corrosion as the destruction of a substance (usually a metal) or its properties because of a reaction with its environment. Methods employed to control corrosion include alteration of the environment, utilization of corrosion resistant materials, cathodic protection, and use of barriers and overdesign (Munger, et. al, 1999). The pros and cons of these techniques are summarized in Table 1. In this paper, focus was directed to corrosion resistant materials in the form of metal alloys and barriers in the form of protective coatings.

Table 1. Comparison of Corrosion Control Method (Munger, et. al, 1999)

METHOD	EXAMPLE	ADVANTAGE	DISADVANTAGE
Altering the Environment	***Changing process paramaters (i.e. P, T)** *** Inhibitors**	**Simple, low cost and retrofit to existing facility.**	**May not completely eliminate problem. Inhibitors are limited to immersion conditions.**
Corrosion Resistant Materials	***Cu, Ni, Cr, Mo alloyed w/ Fe or steel.** *** Thermoplastic materials (i.e. PVS or Polyethylene)**	**Long life span. Applicability is situation specific.**	**High Initial Cost.** **Workability**
Cathodic Protection	***Ship hulls, underwater, underground pipelines.**	**Simplicity. Effective in presence of good electrolytes.**	**Limited usefulness in damp or dry areas. Immersion required.**
Barriers	***Brick Linings** ***Protective coatings, plastic sheeting, monolithic toppings.**	**Most effective and versatile. Reasonable cost.**	**Careful analysis of corrosion problem necessary. Proper surface preparation and application essential.**
Overdesign	***Heavier structural members on thicker plates than required.**		**Neither exact length of life nor replacement cost can be predicted. Higher initial cost. Ineffective. Increased weight.**

Protective coating refers to any liquid, liquefiable or mastic composition that is applied to a surface to protect a substrate from corrosion. Coatings provide protection by one or a combination of three (3) basic mechanisms: barrier, inhibitive or sacrificial. In the geothermal industry, functions of coatings are often times compromised by the dynamic nature and non-uniform chemistry of the geothermal fluids and the harsh operating conditions (i.e. high temperature, high pressure, etc…) of the system. The development of geothermal coating technology is impeded by the small size of the industry but testing in a variety of actual and simulated geothermal conditions can speed-up the process through elimination of inadequate techniques and materials causing accelerated failure. The use of corrosion-resistant coatings will be cost-effective if developed because many of the present materials being considered for the corrosive parts of the geothermal system are expensive (Reeber, 1980).

Metal corrosion is the chemical degradation of metal by its environment. Under particular circumstances of its exposure, metal can be corroded and form either destructive products or have a beneficial effect. Corrosion of metal is influenced by factors that are inherent to the metal alloy (metallurgical, i.e. chemical stability, surface condition, etc…) and by the operating parameters of the industry (environmental, i.e. media solution pH, temperature, pressure, etc…). Optimizing the impacts of metallurgical and environmental factors can control metal corrosion. In the geothermal industry, metal corrosion is a recurring problem because geothermal fluids contain several chemical species (i.e. O, H^+, Cl^-, H_2S, CO_2 species, NH_3, SO_4^{2-}) that are corrosive to most metals when handled at rigorous conditions (i.e. high temperature, high pressure, fast flow rates, etc…). Proper material selection can help minimize the rate of metal corrosion in the geothermal environment. The material selection process incorporates unique considerations such as the dynamic nature of the geothermal fluids, demanding operating conditions of the geothermal industry and metallurgical properties of the chosen alloys.

In this paper, the performances of various types of protective coatings and metal alloys in mitigating corrosion in low-pH geothermal brine ($pH < 4.5$) were evaluated. Different laboratory analyses were performed to measure the corrosion rates and assess the surface quality of the base metal after exposure. The objective was to demonstrate the appropriateness of the laboratory techniques employed in identifying the metal alloys and protective coatings that can potentially be used in immersion conditions with acidic geothermal brine.

2. METHODOLOGY

The experiments in this study were conducted in two stages. The first stage focused on the evaluation of protective coatings while the second stage directed assessments on metal alloys.

2.1 Sample Preparation and Immersion Test Conditions

2.1.1 Protective Coating Evaluation

A total of seven (7) commercially available protective coatings with reported corrosion resistance and application to high temperature systems as well as marine and acidic environments were tested. The characteristics and recommended utilization of each are summarized in Table 2.

Table 2. Characteristics of protective coating samples used in this paper.

BRAND NAME	DESCRIPTION
A	**Epoxy Primer with proprietary components.** Developed for aerospace Al applications with potential use on steel.
B	**Organic.** Rust-inhibiting **acrylic primer** and converter for marine environment.
C	**Epoxy Primer.** Resistant to corrosive chemicals, staining and abrasion with recommended utilization for petrochemical and offshore oil production.
D	**High Temperature Silicone Enamel.** Recommended for high temperature surfaces (649 – 704°C).
E	**High Heat Zinc Modified Primer.** Recommended for high temperature surfaces (454 – 593°C).
F	**CVD material with proprietary components.** Abrasion resistant. High temperature application (450°C). Excellent acid/base pH stability. Chemically inert. Ideal for harsh environments (i.e. offshore/marine, oil and gas, etc...)
G	**CVD multi-layer silicon coating with proprietary components.** Offers effective protection to HCl / HNO_3 and marine environments.

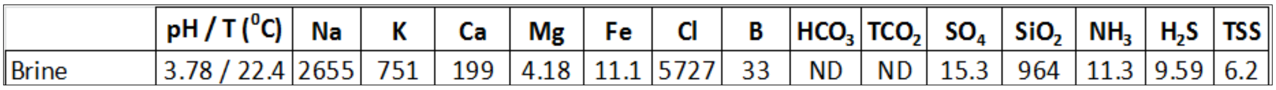
Three (3) types of alloys were used as metal substrates, namely, R46 carbon steel, SS316 and K55. These were polished with increasing grades (i.e. 80, 400, 600, 1500) of SiC paper, sonicated in acetone and dried with N_2 gas prior to coating application. Table 3 details the application method, base metal and effective test area utilized for each protective coating test samples. The actual application method employed for brands B to E were dip coating in an attempt to produce a uniformly coated substrate because the equipments to be used for the recommended coating application method were unavailable at the time of the experiment.

Table 3. Method of coating application used for Brands A to G.

BRAND	APPLICATION METHOD		SUBSTRATE	EFFECTIVE TEST AREA
	RECOMMENDED	ACTUAL		
A	Performed by supplier.		R46, K55	R46 – 9.6 cm²; K55 – 9.6 cm²
B	Brush	Dip Coating	R46	9.6 cm²
C	Airless / Conventional Spray	Dip Coating	R46	9.6 cm²
D	Airless / Conventional Spray	Dip Coating	R46	9.6 cm²
E	Airless / Conventional Spray	Dip Coating	R46	9.6 cm²
F	Performed by supplier.		SS316	6.9 cm²
G	Performed by supplier.		SS316	6.9 cm²

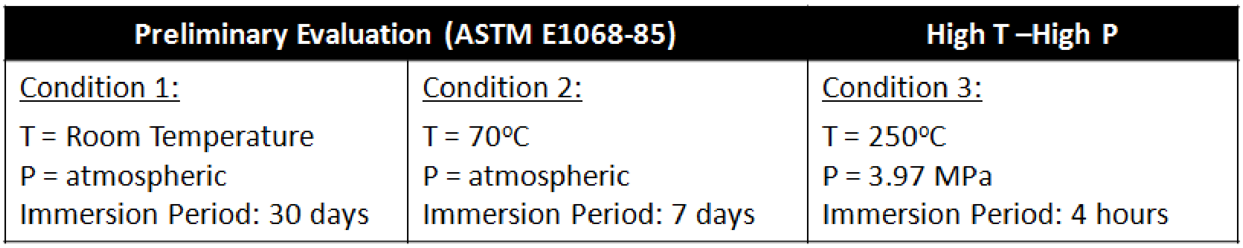
Low-pH geothermal brine fluids sampled from one of the acidic wells in the Greater Tongonan Geothermal Field (GTGF) in Leyte, Philippines were utilized as test media for the immersion trials in this paper. The brine from the acid well has $pH \lesssim 3.5$ at 25°C and is highly mineralized (Table 4). In actuality, it is also subjected to service temperatures ranging from 180°C to 300°C and service pressures spanning from ~0.8 MPag to 13 MPag. The laboratory immersion experiments for the protective coating test samples were performed under three (3) conditions of temperatures and pressures to factor in actual operating environment of acidic geothermal fluids in GTGF (Table 5). Magnetic stirrers were placed inside the vials to incorporate flow dynamics in the immersion test.

Table 4. Chemical composition of the geothermal brine used for testing (in ppm except for pH and T).



	pH / T (^{0}C)	Na	K	Ca	Mg	Fe	Cl	B	HCO_3	TCO_2	SO_4	SiO_2	NH_3	H_2S	TSS
Brine	3.78 / 22.4	2655	751	199	4.18	11.1	5727	33	ND	ND	15.3	964	11.3	9.59	6.2

Table 5. Immersion conditions used for the protective coating evaluation.

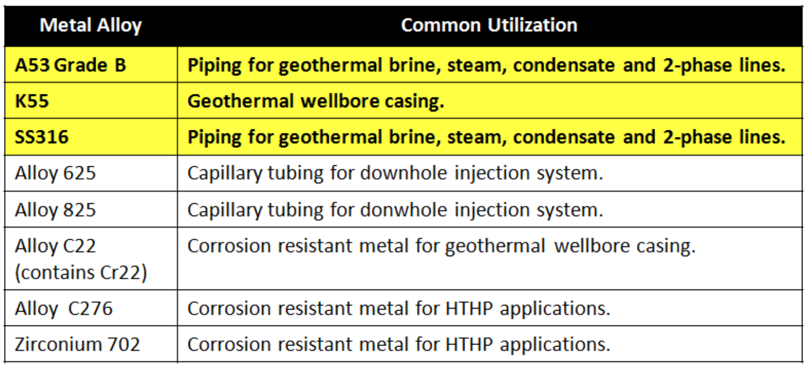


Preliminary Evaluation (ASTM E1068-85)		High T –High P
Condition 1: T = Room Temperature P = atmospheric Immersion Period: 30 days	Condition 2: T = 70°C P = atmospheric Immersion Period: 7 days	Condition 3: T = 250°C P = 3.97 MPa Immersion Period: 4 hours

2.1.2 Metal Alloy Evaluation

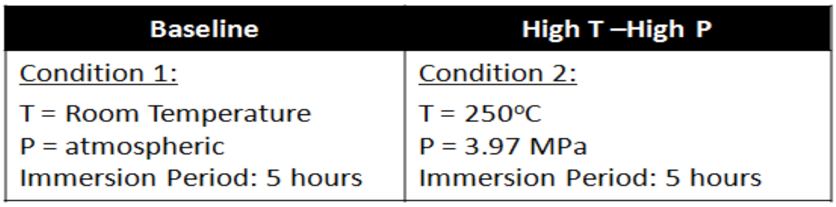
Eight (8) variants of metal alloys were initially identified for evaluation on the bases of current or reported applications in the geothermal industry and of corrosion resistance properties. However, due to time constraints, only the first three metals on Table 6 were experimented in this paper. These were cut into smaller dimensions, polished with increasing grades of SiC paper, sonicated in acetone and dried in N_2 gas before being subjected to two (2) static immersion conditions in low-pH brine for a period of five (5) hours (Table 7).

Table 6. Metal alloys with applications to geothermal industry.



Metal Alloy	Common Utilization
A53 Grade B	**Piping for geothermal brine, steam, condensate and 2-phase lines.**
K55	**Geothermal wellbore casing.**
SS316	**Piping for geothermal brine, steam, condensate and 2-phase lines.**
Alloy 625	Capillary tubing for downhole injection system.
Alloy 825	Capillary tubing for donwhole injection system.
Alloy C22 (contains Cr22)	Corrosion resistant metal for geothermal wellbore casing.
Alloy C276	Corrosion resistant metal for HTHP applications.
Zirconium 702	Corrosion resistant metal for HTHP applications.

Table 7. Immersion conditions used for metal alloy evaluation.



Baseline	High T –High P
Condition 1: T = Room Temperature P = atmospheric Immersion Period: 5 hours	Condition 2: T = 250°C P = 3.97 MPa Immersion Period: 5 hours

2.2 Laboratory Analyses

All test specimens were analyzed before and after immersion in low-pH geothermal brine. The laboratory techniques used and the corresponding objectives are highlighted in Table 8.

Table 8. Analytical techniques used for performance evaluation of coatings and metal alloys.

Analytical Procedure	Purpose
Gravimetric	Metal loss; corrosion rates
Electrochemical Impedance Spectroscopy (EIS)	coating quality
Potentiodynamic Polarization Sweep (PPS)	corrosion rates; failure/corrosion mechanism
Thermogravimetric Analyses (TGA)	characterization of precipitates
X-ray Photoelectron Spectroscopy (XPS)	composition of precipitates/samples
Scanning Electron Microscopy (SEM)	morphology

Baseline PPS and EIS runs were initially performed after the coated substrates were immersed into the acidic test media for ~3 hours. Both PPS and EIS were conducted using platinum as the counter electrode, glass in $Ag/AgCl_{(aq)}$ solution as the reference electrode and the metal substrates / alloys as the working electrodes. A 1M HCl was used as electrolyte during the measurement. The EIS measurements were performed by applying an AC amplitude of 10mV and collecting data from the frequency range of 0.1Hz to $1x10^6$Hz using 7 points per decade. Conversely, the PPS measurements were conducted at a scan rate of 5mV/s and using the potential range of -0.2V to +0.2Vabout the OCP.

Precipitates found suspended in the test media and adhering to the metal surfaces were filtered and dried. These were subjected to TGA and XPS for characterization. Surface morphology of the bare and coated metal alloys was also evaluated visually and through the use of a SEM.

3. RESULTS AND DISCUSSION

3.1 Protective Coating Evaluation

3.1.1 R46 Metal Substrate

The results of the EIS and PPS runs of bare R46 metal showed that this alloy cannot withstand corrosion when exposed to the acidic geothermal test media. Corrosion rates (CRs) obtained for the alloy at Rm. T and 70 °C test conditions were above the 0.12 mm/yr acceptable CR limit used by the GTGF in Leyte (Tables 10 - 12) . The impedance spectra generated for bare R46 metal was also indicative of metal surface corrosion resulting to formation of corrosion products (Figure 1). However, the corrosion products did not seem to offer natural protection since the initially high CR of the alloy during the baseline run at Rm. T. was found to increase further at higher temperature and at longer exposure time. An added protection to the R46 metal must be employed if this alloy will be utilized for immersion conditions in acidic geothermal brine.

EIS and PPS analysis of the coated R46 metal substrates indicated that Brands A, B, C, D and E had inhibitive or protective property against corrosion. Evidence to this was that the impedance spectra of all coating variants tested were capacitive in nature and plotted at higher Z values relative to the bare R46 metal substrate both at Rm. T and at 70 °C test conditions (Figure 1). After 30 days exposure to acidic brine at Rm. T. and atmospheric P, Brand A manifested the least degradation while Brand E showed improved performance. The coating quality of Brands B, C, D and E deteriorated at 70 °C and even further at prolonged exposure.

The protective properties of Brands A, B, C, D and E were also manifested in the PPS spectra obtained for these samples both at Rm. T and 70 °C test conditions (Figure 2). The spectra generally plotted within the area of lower corrosion potential relative to the bare R46 metal. In the case of Brand E, the shift of the PPS spectra from the region with lower E_{corr} and higher Log I values to the area with higher E_{corr} and lower Log I values indicated that its mode of protection was through the formation protective corrosion products. This mechanism was also demonstrated by Brand B but only at the higher temperature condition of 70 °C. Deterioration of coating performance as evidenced by the shift in the spectra to the lower E_{corr} region was observed for Brands B, C and D after 30 days exposure to acidic brine at Rm. T and atm. P condition and for Brands C and D after 7 days exposure to same acidic test media but at 70 °C and atm. P.

The protective properties of the coating samples were quantified via calculation of protection efficiencies (PE) and CR (Table 10 – 12). At Rm. T and atm. P condition, the PEs of Brands A to E were calculated to be above 85% even after 30 days exposure to the acidic test fluids. Highest PEs (~97%) were obtained for samples coated with Brands C and D while the smallest PE (~88%) was recorded for Brand A. Measured CR for all test variants were below the 0.12 mm/yr acceptable CR limit. Except for Brand D which generated 95% PE, low PEs (55-68%) were recorded for Brands B, C and E upon exposure to acidic geothermal brine at higher T of 70 °C and atm. P. Slight improvement in PEs were noticed after 7 days but these were all below 80% PE. Measured CRs for Brands B, C, D and E at this test condition breached the 0.12 mm/yr acceptable CR limit.

Precipitates were found suspended in the acidic geothermal brine test solution after the coating immersion tests were performed. TGA identified these to be inorganic in nature (Figure 3). Further test by XPS revealed that O, Si, and C were the major elemental components with minimal concentration of some metals. The Fe detected in the precipitates may have come from the Fe components of the acidic geothermal brine test media or to a lesser extent from the underlying R46 metal substrate.

SEM images (Figures 4 and 5) obtained for the coated substrates prior exposure to acidic geothermal brine test media revealed that coating application via the dip coating method resulted to coating defects such as wrinkling in the case of Brand C. Cratering or pinholing was likewise observed for Brand B which signified either thick application of coating or improper mixing of coating components.

3.1.2 SS316 Metal Substrate

SS316 showed better resistance to corrosion in acidic geothermal brine as compared to the R46 metal alloy. Its impedance spectra relatively had a capacitive behavior and plotted within the higher Log Z values (Figure 6). Its PPS spectra also plotted within the higher E_{corr} and lower Log I values common to samples with low corrosion rates and low corrosion potential (Figure 7). Measured CRs for the SS316 bare metal were below the 0.12 mm/yr acceptable CR limit and lower in comparison to that of the bare R46 metal. However, an increase in measured CR was observed after 7 days exposure to geothermal acidic brine at 70 °C and atm P condition with no manifestation of likely formation of corrosion products detected in the impedance spectra (Tables 13 and 14). This meant that an added protection against corrosion must still be applied to ensure that SS316 can withstand prolonged exposure to acidic geothermal brine.

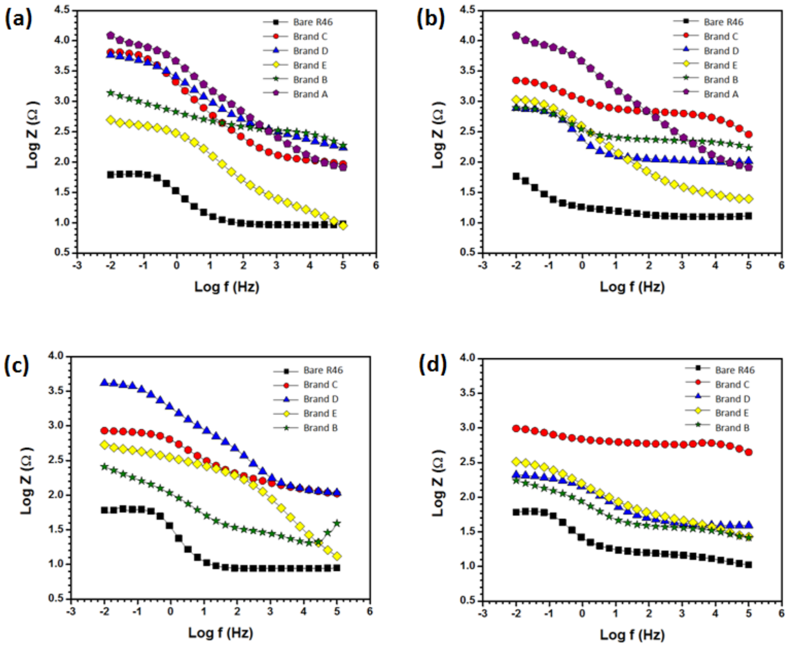


Figure 1. Impedance spectra of bare and coated R46 metals substrates: (a) baseline after 3 hours immersion at Rm.T-atm. P condition; (b) after 30 days immersion at Rm. T-atm P condition; (c) baseline after 3 hours immersion at 70 deg C-atm. P conditionl (d) after 7 days immersion at 70 deg C-atm. P condition.

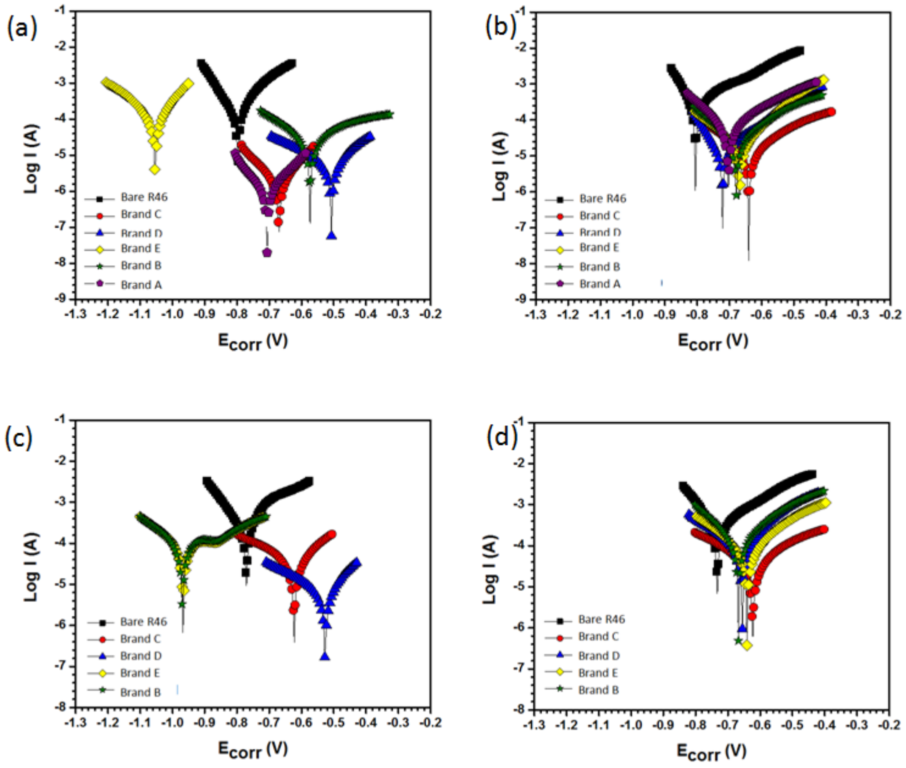


Figure 2. PPS spectra of bare and coated R46 metal substrates: (a) baseline after 3 hours immersion at Rm.T-atm. P condition; (b) after 30 days immersion at Rm. T-atm P condition; (c) baseline after 3 hours immersion at 70 deg C-atm. P conditionl (d) after 7 days immersion at 70 deg C-atm. P condition.

Table 9. Baseline PPS results of bare and coated R46 metal at Rm. T-atm. P.

Product	Rp (Ohm)	b_c (V/dec)	b_a (V/dec)	E_{corr} (V)	I_{corr} (A)	Corrosion Rate (mm/yr)	Protection Efficiency (%)
Bare R46	1.24 x 10^{2}	0.179	0.107	-0.797	2.33 x 10^{-4}	0.2820	-
Brand C	1.22 x 10^{4}	0.199	0.180	-0.670	3.37 x 10^{-6}	0.0041	98.55
Brand D	5.48 x 10^{3}	0.879	0.208	-0.507	1.33 x 10^{-5}	0.0161	94.29
Brand E	2.43 x 10^{2}	0.139	0.093	-1.05 0	9.98 x 10^{-5}	0.1210	57.17
Brand B	1.36 x 10^{3}	0.277	0.361	-0.574	5.00 x 10^{-5}	0.0605	78.54
Brand A	1.88 x 10^{4}	0.306	0.228	-0.706	3.02 x 10^{-6}	0.0040	98.70

Table 10. PPS results of bare and coated R46 metal at Rm. T-atm. P.

Product	Rp (Ohm)	b_c (V/dec)	b_a (V/dec)	E_{corr} (V)	I_{corr} (A)	Corrosion Rate (mm/yr)	Protection Efficiency (%)
Bare R46	4.73 x 10^{1}	0.100	0.387	-0.784	7.31 x 10^{-4}	0.8840	-
Brand C	2.51 x 10^{3}	0.239	0.266	-0.640	2.18 x 10^{-5}	0.0264	97.02
Brand D	1.66 x 10^{3}	0.116	0.215	-0.721	1.97 x 10^{-5}	0.0239	97.31
Brand E	1.28 x 10^{3}	0.185	0.179	-0.669	3.08 x 10^{-5}	0.0373	95.79
Brand B	1.09 x 10^{3}	0.177	0.228	-0.679	3.96 x 10^{-5}	0.0479	94.58
Brand A	4.69 x 10^{2}	0.156	0.217	-0.703	8.41 x 10^{-5}	0.1017	88.50

Table 11. Baseline PPs results of bare and coated R46 metal at 70 °C-atm. P.

Product	Rp (Ohm)	b_c (V/dec)	b_a (V/dec)	E_{corr} (V)	I_{corr} (A)	Corrosion Rate (mm/yr)	Protection Efficiency (%)
Bare R46	9.00×10^{1}	0.154	0.108	-0.772	3.14×10^{-4}	0.3790	-
Brand C	9.51×10^{2}	0.681	0.321	-0.623	9.97×10^{-5}	0.1210	68.25
Brand D	4.50×10^{3}	0.785	0.181	-0.527	1.42×10^{-5}	0.0172	95.48
Brand E	3.33×10^{2}	0.157	0.345	-0.967	1.41×10^{-4}	0.1710	55.10
Brand B	3.51×10^{2}	0.133	0.243	-0.676	1.06×10^{-4}	0.1290	66.24

Table 12. PPS results of bare and coated R46 metal at 70 °C-atm P.

Product	Rp (Ohm)	b_c (V/dec)	b_a (V/dec)	E_{corr} (V)	I_{corr} (A)	Corrosion Rate (mm/yr)	Protection Efficiency (%)
Bare R46	8.64×10^{1}	0.123	0.288	-0.734	4.33×10^{-4}	0.5240	-
Brand C	1.03×10^{3}	0.412	0.414	-0.624	8.73×10^{-5}	0.1060	79.84
Brand D	3.48×10^{2}	0.255	0.158	-0.655	1.22×10^{-4}	0.1470	71.82
Brand E	4.41×10^{2}	0.260	0.252	-0.641	1.26×10^{-4}	0.1520	70.90
Brand B	2.37×10^{2}	0.229	0.312	-0.667	2.42×10^{-4}	0.2930	44.11

Only Brands F and G were applied to SS316 metal substrates among the seven (7) coating variants experimented in this paper. Results of the EIS and PPS runs on these two (2) coating brands indicated that both had protective or inhibitive property against corrosion in an acidic geothermal environment (Figures 6 and 7). Impedance spectra of Brands F and G demonstrated capacitive behavior with higher log Z values than the bare SS316 metal substrate both at Rm. T and 70 °C immersion conditions. The inhibitive property and the coating quality of Brand F and G were also maintained even after 1 month exposure to acidic geothermal brine at Rm. T condition. However, a decline in protective property was noted after exposure to acidic geothermal brine at 70 °C and atm. P, especially after 7 days of immersion.

The PPS spectra showed that both Brands F and G have lower to comparable resistance to bare SS316 metal upon initial contact with acidic geothermal brine at Rm. T and atm. P condition (Figure 7). The shift in the PPS spectra to the higher E_{corr} and lower log I region after 30 days exposure to acidic brine at Rm. T meant that Brands F and G worked by acting as sacrificial anodes that undergo corrosion to form corrosion products that would protect the SS316 metal from further degradation. The PPS spectra of both Brands F and G stagnated in the region of E_{corr} values ranging from -0.4 V to -0.02 V even after prolonged exposure to acidic geothermal brine at higher temperature of 70 °C which was just comparable to the performance of bare SS316 metal.

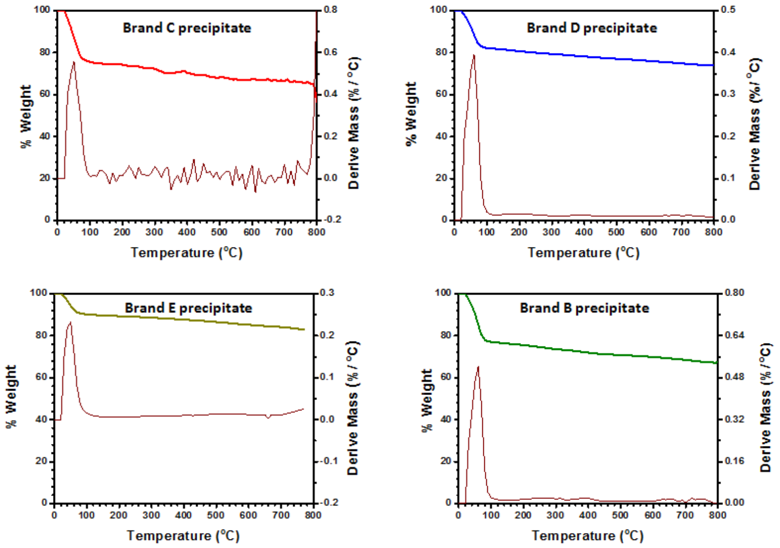


Figure 3. TGA results of precipitates found suspended in the acidic geothermal brine at 70 deg C-atm. P condition where bare and coated R46 metal substrate were exposed.

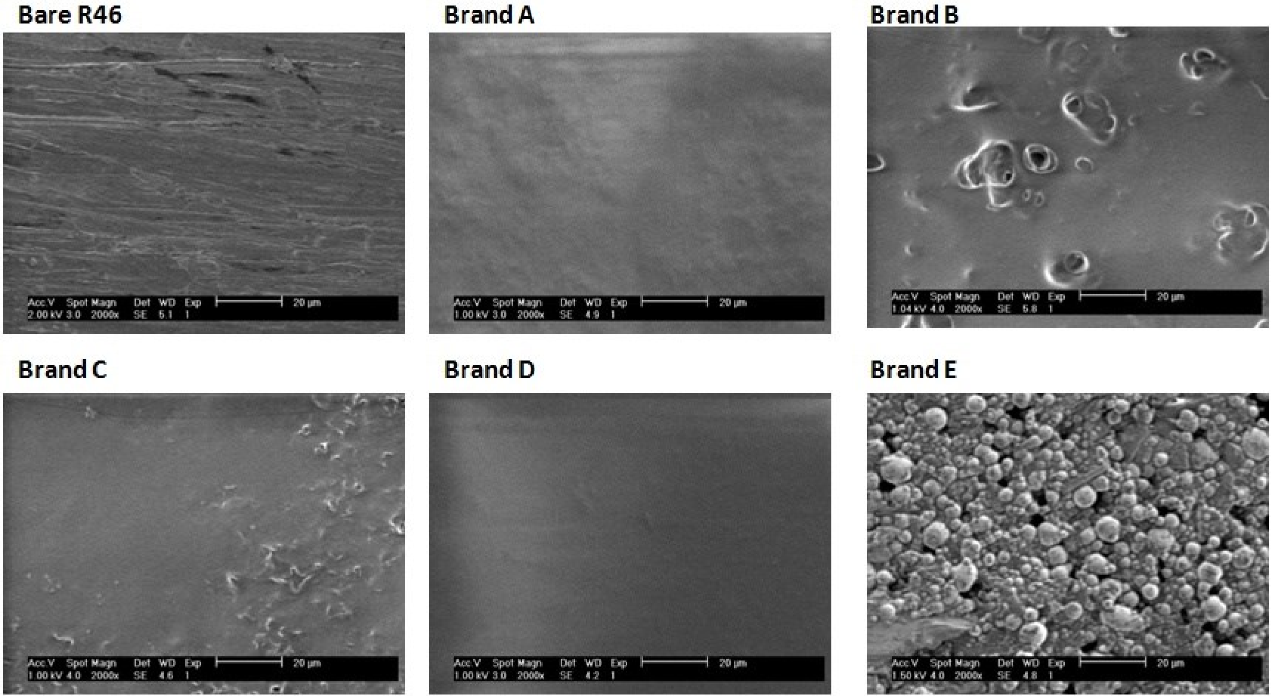


Figure 4. SEM images at 2000X magnification (20µm scale) of bare R46 and coated R46 substrates before exposure to acidic geothermal brine.

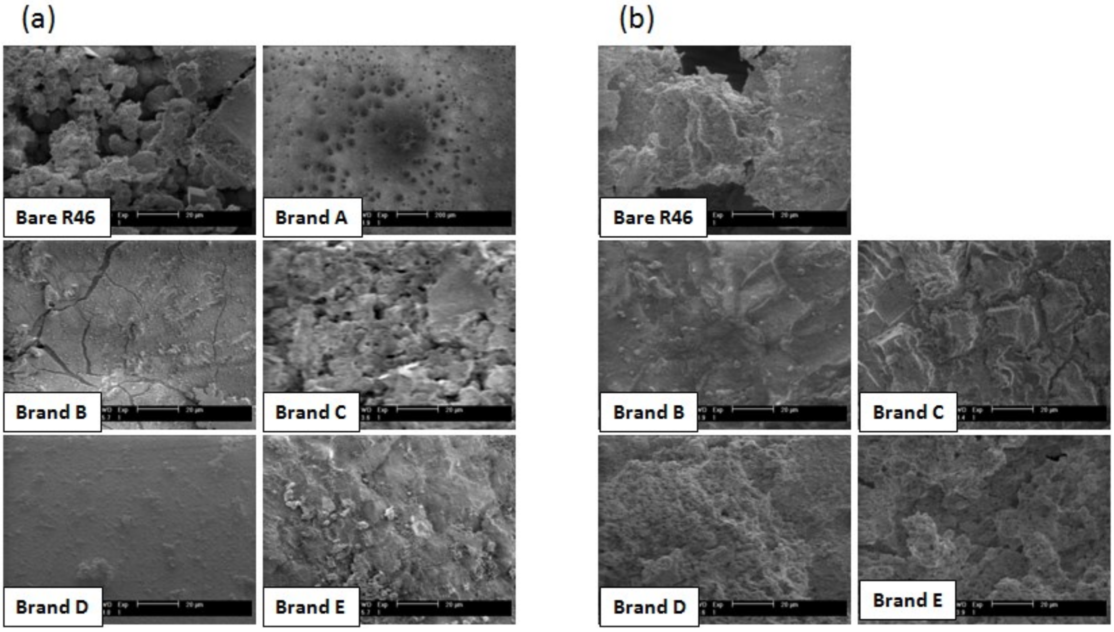


Figure 5. SEM images at 2000X magnification (20µm scale) of bare R46 and coated R46 substrates (a) after 30 days exposure to acidic geothermal brine Rm. T-atm. P; (b) after 7 days exposure to acidic geothermal brine at 70 °C-atm. P.

The measured CRs for SS316 substrate coated with Brands F and G were below the 0.12 mm/y acceptable CR and lower than those obtained for Brands A, B, C, D and E. Calculated PEs for Brand G were low (~40 to 50%) after prolonged exposure to acidic brine both at Rm. T and 70 °C (Tables 13 and 14). Higher PEs (>85%) were calculated for Brand F, both at Rm. T and 70 °C test conditions, but a noticeable drop in PE was observed after prolonged exposure to the acidic test media. Brand F was further exposed to acidic geothermal brine at HTHP conditions to evaluate if its high PE will be sustained. However, after 5 hours exposure to brine at 250 °C and 3.97 MPa, the capacitive behavior of the impedance spectra was no longer observed and PPS spectra shifted to the higher corrosion potential region (Figure 10). The calculate PE also dropped to ~36% (Figure 11).

Suspended particles were not found in the test solutions where the SS316 metal coated with Brand F and G were immersed. SEM images of Brand F coated substrates after exposure to low-pH brine at 70 °C and 250 °C revealed comparable surface morphology to bare SS316 metal (Figure 8 and 12). However, surface cracking was note for Brand F coated substrate exposed to acidic brine at Rm. T condition for 30 days.

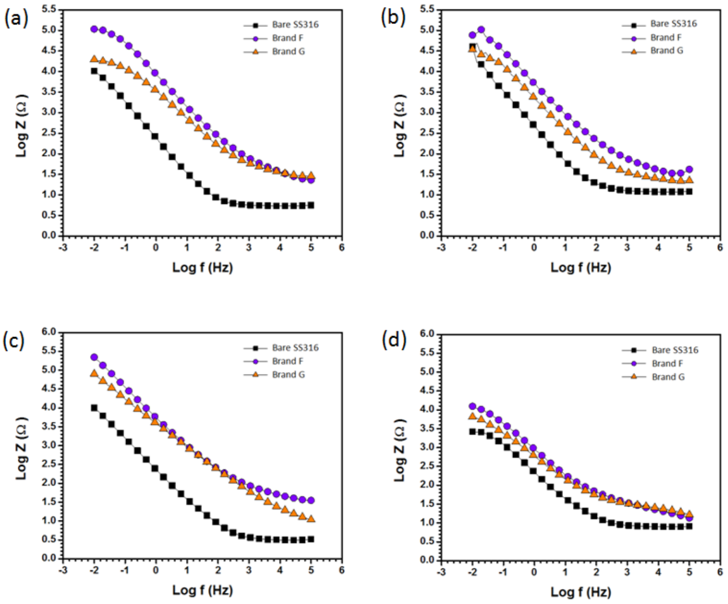


Figure 6. Impedance spectra of bare and coated SS316 metals substrates: (a) baseline after 3 hours immersion at Rm.T-atm. P condition; (b) after 30 days immersion at Rm. T-atm P condition; (c) baseline after 3 hours immersion at 70 deg C-atm. P conditional (d) after 7 days immersion at 70 deg C-atm. P condition.

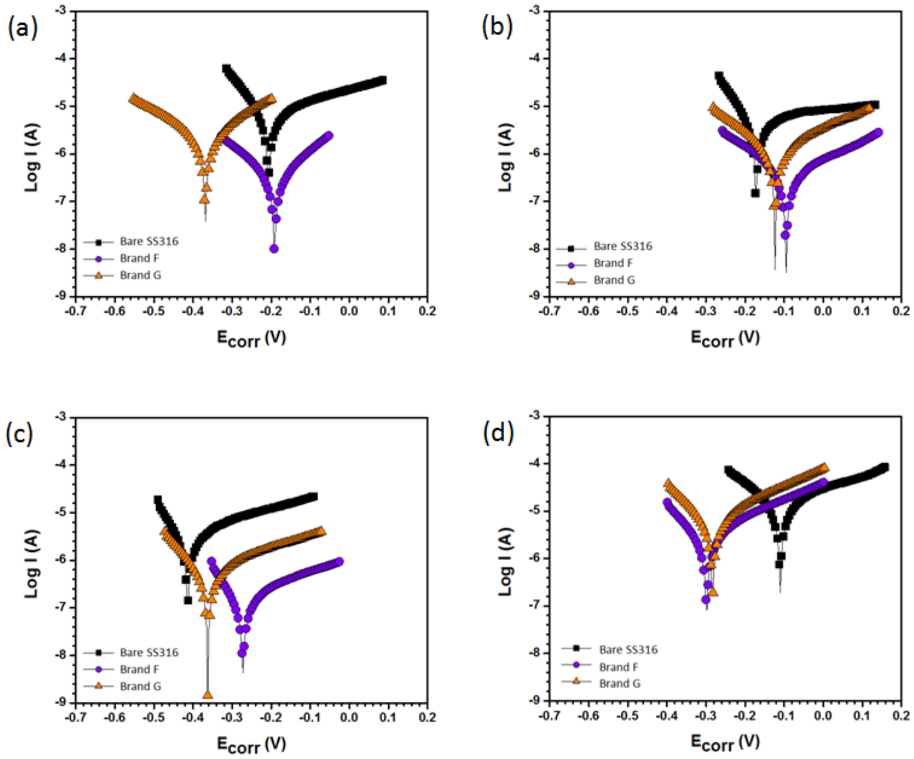
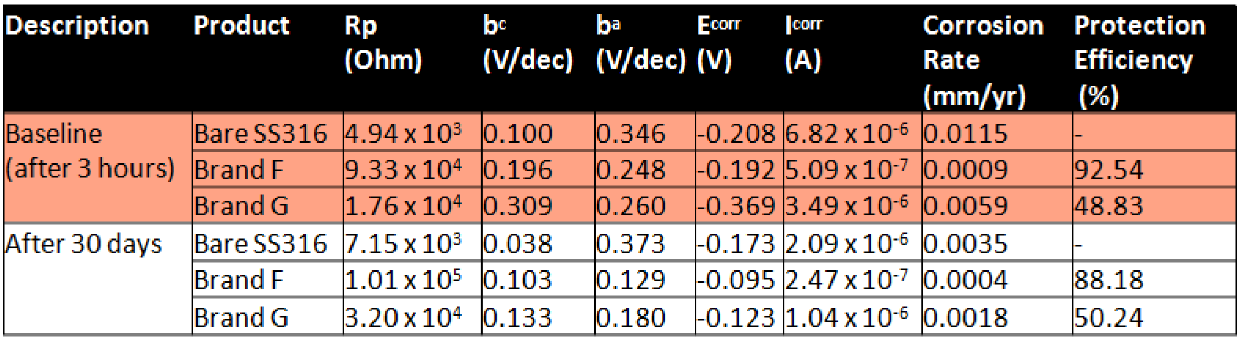


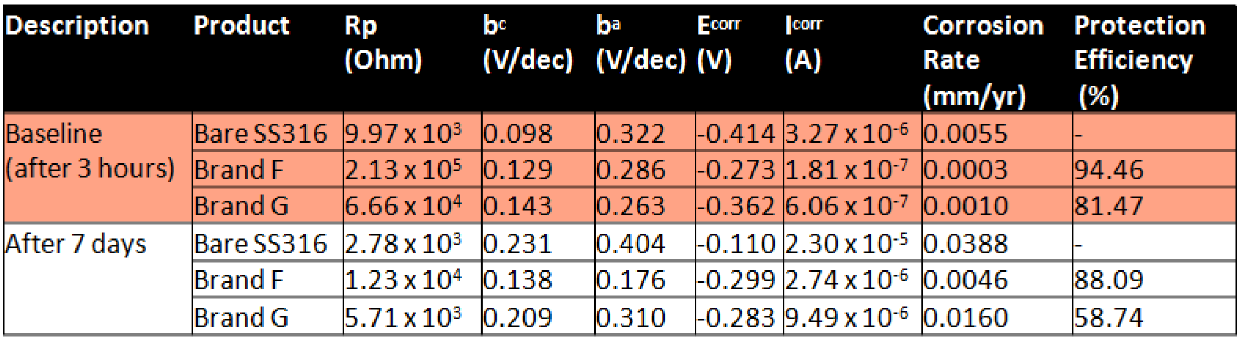
Figure 7. PPS spectra of bare and coated SS316 metals substrates: (a) baseline after 3 hours immersion at Rm.T-atm. P condition; (b) after 30 days immersion at Rm. T-atm P condition; (c) baseline after 3 hours immersion at 70 deg C-atm. P conditional (d) after 7 days immersion at 70 deg C-atm. P condition.

Table 13. PPS results of bare and coated SS316 metal at Rm. T-atm. P.

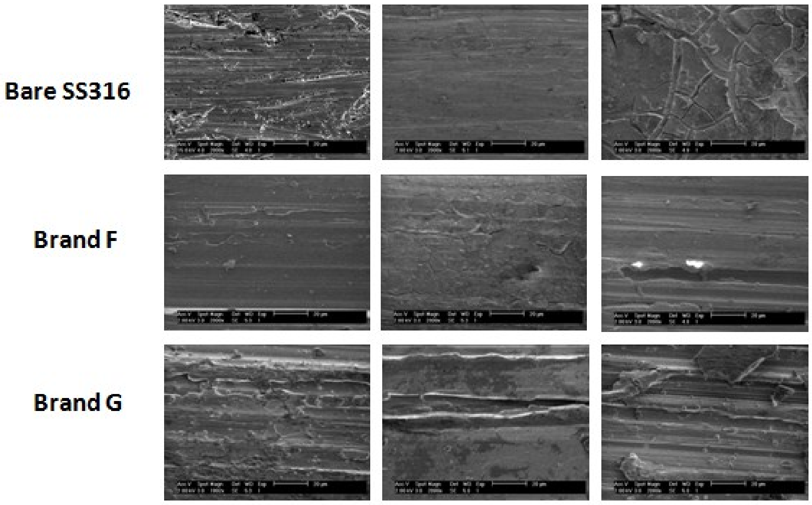


Description	Product	Rp (Ohm)	bc (V/dec)	ba (V/dec)	Ecorr (V)	Icorr (A)	Corrosion Rate (mm/yr)	Protection Efficiency (%)
Baseline (after 3 hours)	Bare SS316	4.94×10^3	0.100	0.346	-0.208	6.82×10^{-6}	0.0115	-
	Brand F	9.33×10^4	0.196	0.248	-0.192	5.09×10^{-7}	0.0009	92.54
	Brand G	1.76×10^4	0.309	0.260	-0.369	3.49×10^{-6}	0.0059	48.83
After 30 days	Bare SS316	7.15×10^3	0.038	0.373	-0.173	2.09×10^{-6}	0.0035	-
	Brand F	1.01×10^5	0.103	0.129	-0.095	2.47×10^{-7}	0.0004	88.18
	Brand G	3.20×10^4	0.133	0.180	-0.123	1.04×10^{-6}	0.0018	50.24

Table 14. PPS results of bare and coated SS316 metal at 70 deg.C-atm. P.



Description	Product	Rp (Ohm)	bc (V/dec)	ba (V/dec)	Ecorr (V)	Icorr (A)	Corrosion Rate (mm/yr)	Protection Efficiency (%)
Baseline (after 3 hours)	Bare SS316	9.97×10^3	0.098	0.322	-0.414	3.27×10^{-6}	0.0055	-
	Brand F	2.13×10^5	0.129	0.286	-0.273	1.81×10^{-7}	0.0003	94.46
	Brand G	6.66×10^4	0.143	0.263	-0.362	6.06×10^{-7}	0.0010	81.47
After 7 days	Bare SS316	2.78×10^3	0.231	0.404	-0.110	2.30×10^{-5}	0.0388	-
	Brand F	1.23×10^4	0.138	0.176	-0.299	2.74×10^{-6}	0.0046	88.09
	Brand G	5.71×10^3	0.209	0.310	-0.283	9.49×10^{-6}	0.0160	58.74



Before exposure to acidic geothermal brine.

Post-exposure to acidic geothermal brine at room temperature and atm P condition.

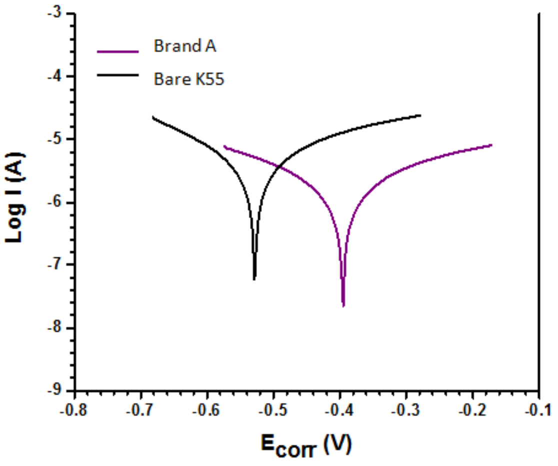
Post-exposure to acidic geothermal brine at T = 70°C and atm P condition.

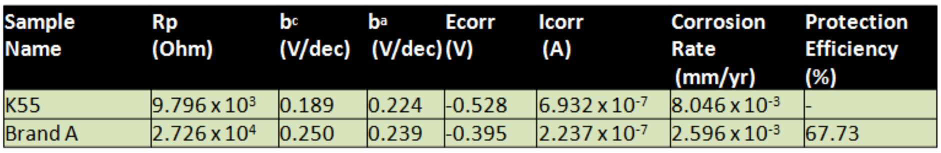
Figure 8. SEM images at 2000 magnification (20µm scale) of bare and coated SS316 metal substrates.

3.1.3 K55 Metal Substrate

The K55 metal substrate was coated using only Brand A and was tested only in acidic geothermal brine at HTHP condition. Impedance spectra obtained for the sample showed limited protective property for Brand A at HTHP condition. Baseline impedance spectra (~3 hours exposure to HTHP condition) barely showed capacitive behavior but plotted along high Log Z values than bare K55 metal. The protective property of Brand A at HTHP condition was also manifested in the shift of the PPS spectra for Brand A to higher E_{corr} and lower Log I values (Figure 9). Measured CR for Brand A coated K55 metal was lower than that obtained for bare

K55 metal alloy but calculated PE was only 67.7%. Impedance spectra after 5 hours exposure to HTHP condition showed significant deterioration in Brand A's coating quality. This was validated by SEM images wherein portions of the coating appeared to have reacted with the acidic geothermal brine test media thereby giving it a cracked like texture.





Sample Name	Rp (Ohm)	b_c (V/dec)	b_a (V/dec)	Ecorr (V)	Icorr (A)	Corrosion Rate (mm/yr)	Protection Efficiency (%)
K55	9.796×10^{3}	0.189	0.224	-0.528	6.932×10^{-7}	8.046×10^{-3}	-
Brand A	2.726×10^{4}	0.250	0.239	-0.395	2.237×10^{-7}	2.596×10^{-3}	67.73

Figure 9. PPS results of bare and coated K55 metal substrate after exposure to acidic brine at HTHP.

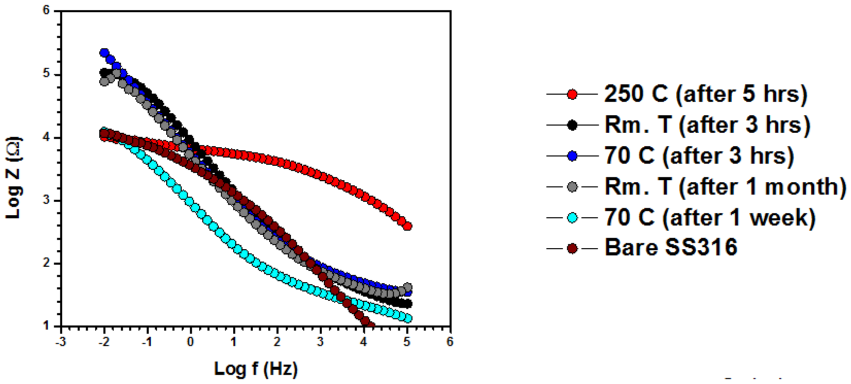
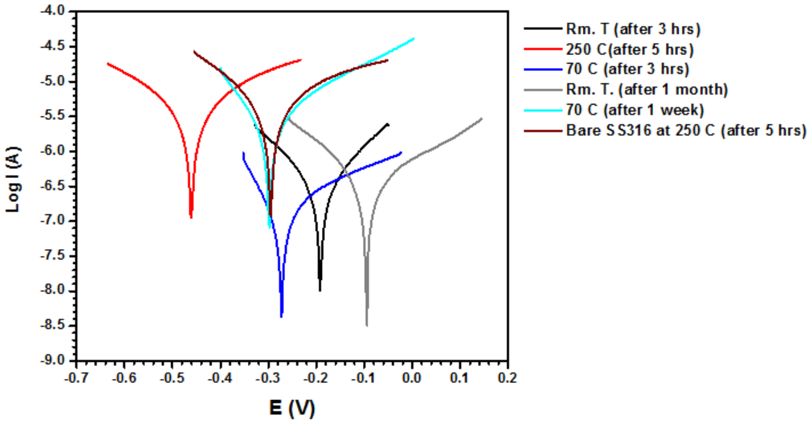


Figure 10. EIS spectra of Brand F after immersion in acidic geothermal brine at different temperatures.



Sample Name	Rp (Ohm)	b_c (V/dec)	b_a (V/dec)	Ecorr (V)	Icorr (A)	Corrosion Rate (mm/yr)	Protection Efficiency (%)
Bare SS316	9.243×10^{3}	0.215	0.335	-0.295	8.923×10^{-7}	1.038×10^{-2}	-
Brand F 250 C	1.128×10^{4}	0.205	0.206	-0.461	5.732×10^{-7}	6.671×10^{-3}	35.76

Figure 11. PPS results of Brand F after immersion in acidic geothermal brine at different temperatures.

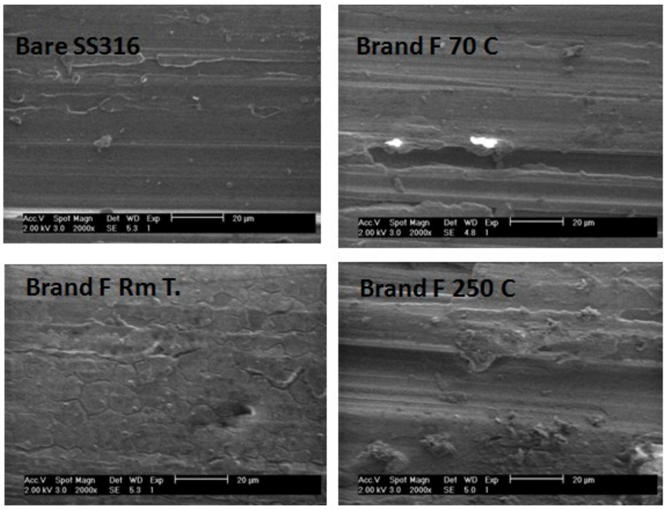


Figure 12. SEM images at 2000X magnification (20µm scale) for Brand F.

3.2 Metal Alloys Evaluation

Only three (3) types of metal alloys (SS316, K55 and A53 Grade B) were experimented in this paper. Results of the gravimetric analysis (Table 15) showed metal loss for SS316 alloy after exposure to acidic geothermal brine both at Rm. T-atm. P and HTHP conditions which was indicative of an active corrosion process. The measured CR of SS316 alloy increased significantly from 0.012 mm/yr to 0.617 mm/yr upon exposure to HTHP condition. Consequently, metal gains observed for K55 and A53 Grade B alloys suggested the formation of scales on the metal surface, likely by-products of a corrosion process. CRs of these two (2) alloys also increased after exposure to HTHP condition.

Table 15. Results of Gravimetric analyses for SS316, K55 and A53 Gr. B after exposure to acidic geothermal brine.

Immersion Condition	Alloy	Mass Before Immersion (g)	Mass After Immersion (g)	Metal Loss (g)	Density (g/cm^2)	Area (cm^2)	Exposure Time (hrs)	Corrosion Rate (mm/yr)
(I) Room Temp., atm P	SS316	9.9190	9.9189	+0.0001	7.85	11.8	5	+0.0126
	A53 GrB	4.0526	4.0571	-0.0044	7.87	7.26	5	-1.3579
	K55	3.9250	3.9321	-0.0072	7.86	7.26	5	-2.1978
(II) T = 250°C, P = 3.97 Mpa	SS316	9.8762	9.8729	+0.0033	7.85	11.8	5	+0.6172
	A53 GrB	4.1653	4.1664	-0.0011	7.87	7.26	5	-0.3369
	K55	3.9238	3.9242	-0.0004	7.86	7.26	5	-0.1124

The impedance spectra of SS316 alloy after exposure to Rm. T-atm. P condition showed capacitive behavior and plotted at higher Log Z values compared to the K55 and A53 Gr. B metals (Figure 13). However, this was not sustained at HTHP condition as the spectra shifted to lower Log Z values suggestive of surface degradation. The impedance spectra of K55 and A53 Gr. B alloys at HTHP condition plotted at higher Log Z values indicative of enhanced surface protection.

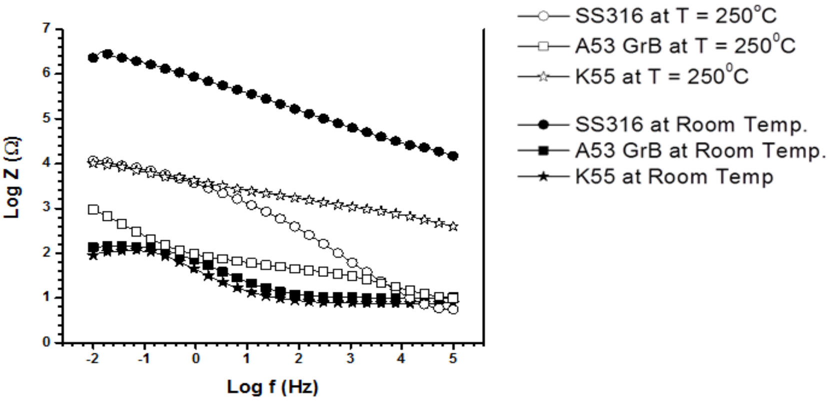
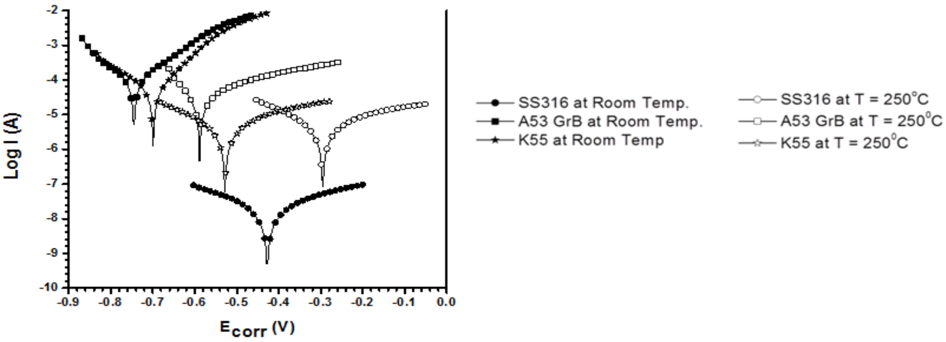


Figure 13. Impedance spectra of SS316, K55 and A53 Gr. B alloys after exposure to acidic geothermal brine.



Immersion Condition	Alloy	Rp (Ohm)	b^c (V/dec)	b^a (V/dec)	Ecorr (V)	Icorr (A)	Corrosion Rate (mm/yr)
(I) Room Temp., atm P	SS316	2.464×10^6	0.318	0.433	-0.428	4.684×10^{-9}	5.451×10^{-5}
	A53 GrB	2.123×10^2	0.120	0.150	-0.751	2.032×10^{-5}	2.359×10^{-1}
	K55	4.195×10^2	0.243	0.146	-0.699	1.411×10^{-5}	1.638×10^{-1}
(II) T = 250°C, P = 3.97 Mpa	SS316	9.243×10^3	0.215	0.335	-0.295	8.923×10^{-7}	1.038×10^{-2}
	A53 GrB	9.027×10^2	0.106	0.213	-0.604	5.088×10^{-6}	5.906×10^{-2}
	K55	9.796×10^3	0.189	0.224	-0.528	6.932×10^{-7}	8.046×10^{-3}

Figure 14. PPs results of SS316, K55 and A53 Gr. B alloys after exposure to acidic geothermal brine.

The PPS spectra of all three (3) alloys after exposure to HTHP condition showed a shift towards the lower E_{corr} values relative to those spectra obtained after exposure to Rm. T-atm. P condition (Figure 14). However, measured CR for SS316 alloy still increased at HTHP because its spectra at 250 °C plotted towards a higher I_{corr} value. The K55 and A53 Gr. B alloys performed better at HTHP condition since these generated spectra that plotted towards lower I_{corr} and higher E_{corr} relative to Rm. T. condition. The values obtained for the Tafel constants of these two (2) alloys indicated that at HTHP, corrosion is controlled by the increase in anodic reaction and a decrease in cathodic reaction. Although an increase in CRs was noted for K55 and A53 Gr. B alloys at HTHP, the increase in SS316 CR was still more substantial.

Reddish brown precipitates were found suspended in the acidic geothermal brine test media where the three (3) alloys were immersed at 250 °C and 3.7 MPag for ~5 hours. XPS analysis identified these precipitates to be composed of O, Si, Cl, and C with traces of Fe and Ca. These are elemental components of oxides, silica, inorganic salts and carbonates that are usually found as scale components in geothermal pipe lines. Visual inspection of the metal alloys revealed the presence of brownish –black scale deposits on the surface of A53GrB and K55 metal alloys after exposure to acidic brine at Rm. T. which were also observed at HTHP environment. XPS analysis of the metal surfaces also indicated the presence of O, Si and Cl (Figure 15). SEM analyses of the SS316 alloy showed minimal corrosion damage at Rm. T-atm P but with minute amount of precipitates at HTHP (Figure 16). SEM images of both K55 and A53GrB alloys exhibited presence of precipitates on the surface after exposure to acidic brine at Rm. T and HTHP conditions (Figure 17 and 18). These appeared to have limited adherence and showed a rough, irregular, porous morphology with finer grains at HTHP. This meant that the corrosion products formed on the surface were not sufficient barriers to prevent metal contact with the corrosive acidic geothermal brine.

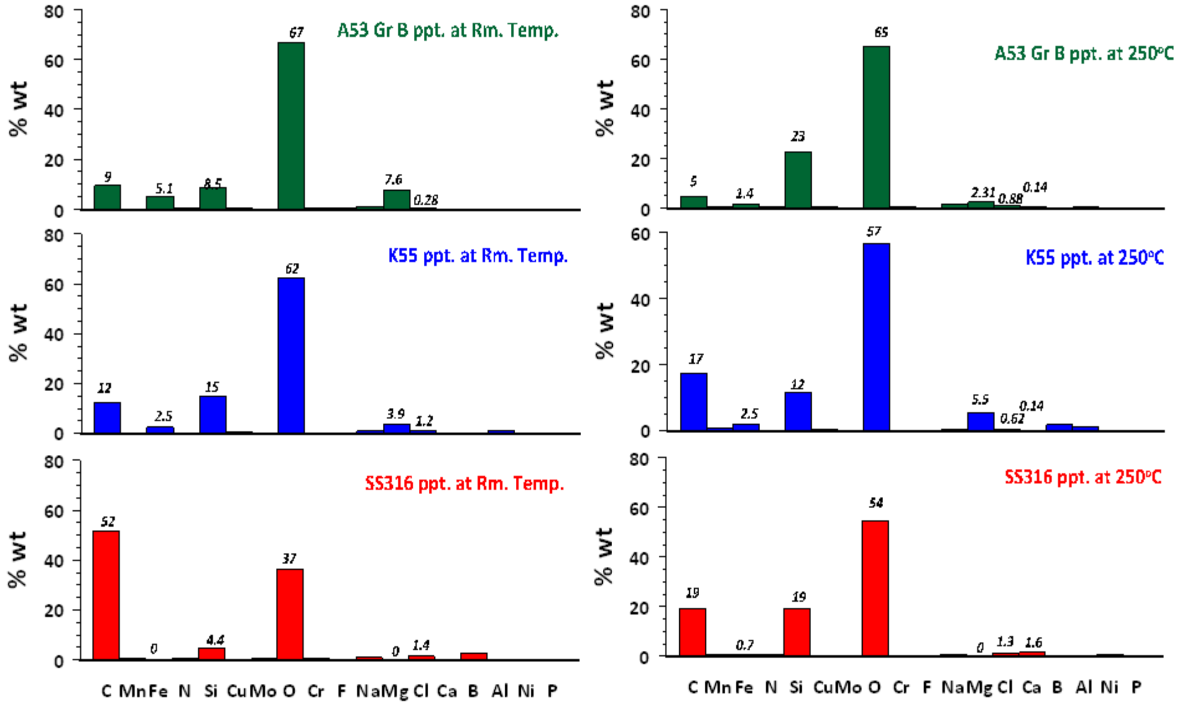
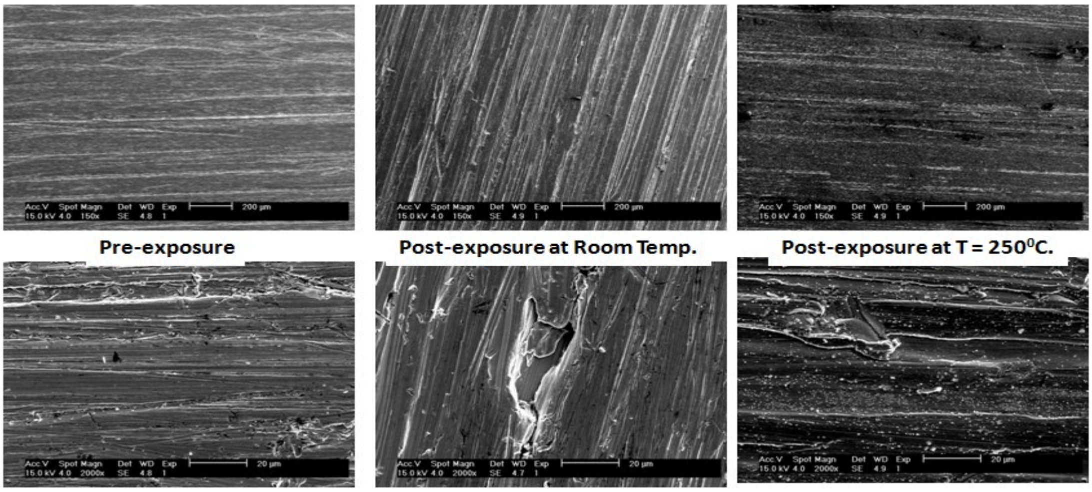


Figure 15. XPS results of adherent precipitates on the surface of SS316, K55 and A53 gr. B alloys after exposure to acidic geothermal brine.


Pre-exposure

Post-exposure at Room Temp.

Post-exposure at T = 250°C.

Figure 16. SEM images (20µm scale) of SS316 metal at 150X (top) and 2000X (bottom) magnifications before and after exposure to acidic geothermal brine.

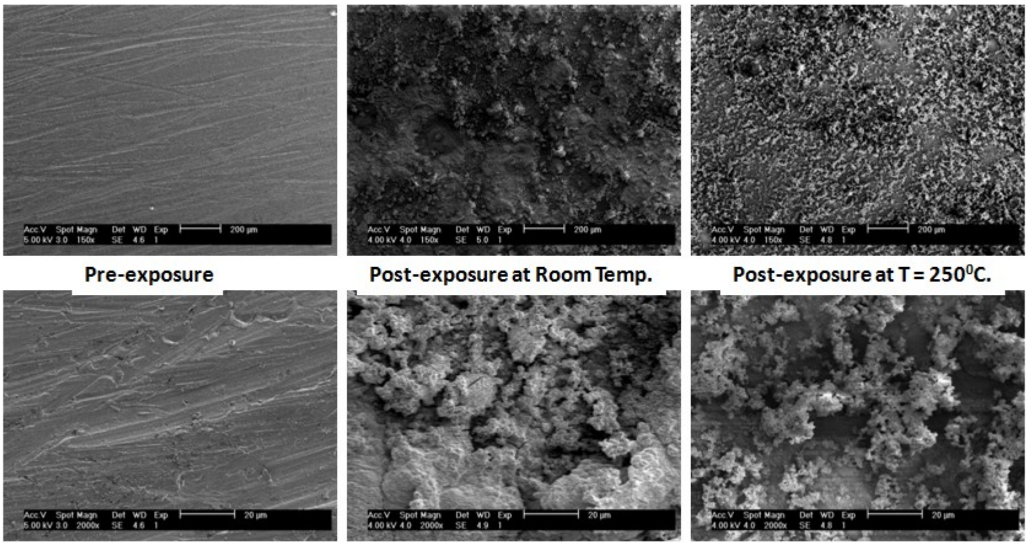


Figure 17. SEM images (20µm scale) of A53 Gr. B metal at 150X (top) and 2000X (bottom) magnifications before and after exposure to acidic geothermal brine.

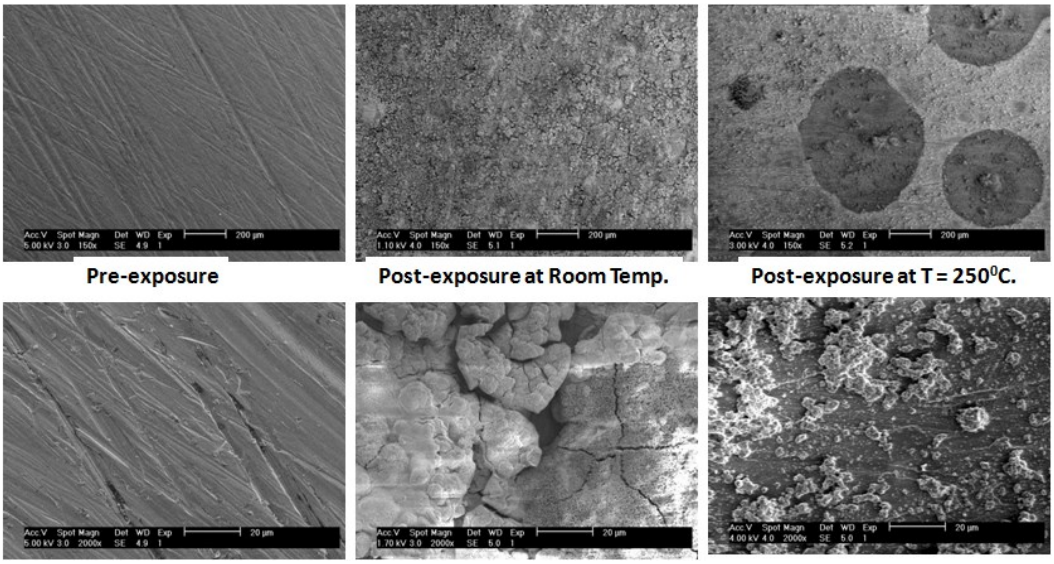


Figure 18. SEM images (20µm scale) of K55 metal at 150X (top) and 2000X (bottom) magnifications before and after exposure to acidic geothermal brine.

4. CONCLUSION

The following conclusions can be said on the performance of the coating and metal alloys tested in this paper:

(1) Brands A, B, C, D, E, F and G have protective properties and can potentially be applied to immersion conditions in acidic geothermal brine at Rm. T-atm. P condition. If utilized, life span may be limited and utilization may induce deposition of silica,oxides and inorganic salts inside the pipelines.

(2) Only Brand F has the potential utilization for immersion conditions at relatively higher service temperature of 70 deg C. However, life span may be limited as it is expected to deteriorate through time and continued use may result to deposition of silica, inorganic salts and oxides along the pipe lines.

(3) Dip coating is not a suitable method for application of Brands B, C, D and E as this will result to coating defects such as wrinkling and pinholing. Recommended application technique in the MSDS must be followed.

(4) SS316 metal alloy is less favored for use as casing material for acidic wellbores because it will result to high corrosion rates. The minute precipitates formed during its exposure to HTHP condition did not seem to offer further corrosion protection.

(5) Corrosion rates of SS316, K55 and A53GrB were found to increase with temperature. This suggests that CR may further increase if exposure period to HTHP condition is prolonged.

(6) K55 and A53 Gr. B alloys are more suitable casing materials for use at HTHP condition in wells discharging acidic geothermal brine. However, the corrosion products formed on the surface of these alloys will only act as temporary protection as these are relatively porous in nature.

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